SMAll ANGLE NEUTRON SCATTERING STUDIES OF COAL-EXTRACT SOLUTIONS

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key words *SANS, Coal Extracts, Fractals*

INTRODUCTION

Interest in the physics and chemistry of coal extracts has extended for over 100 years. Early on it was recognized that pyridine was a particularly good solvent capable of extracting a significant weight percent of intermediate rank coals. Many of the current theories regarding the macromolecular structure of coals (type III kerogens) are based on the fact that there exists a physically definable limit in the extractability of soluble organics from coal in pyridine[1]. The non-extractable residue is generally considered to be a cross-linked macromolecular network[2]. The extract-solvent "solutions", although acknowledged to be far from ideal (thermodynamically), are presumed to be "molecular solutions" in the sense that random mixing of the constituents occurs within a single solution phase[3].

Recently, a number of investigations have challanged this established model of coal structure. In particular, studies by Iino and colleagues[4],using mixed solvent systems (most notably, a n-methyl-2-pyrrolidinone (NMP) mixture with CS_2), have demonstrated increases in extractabilities of more than twice that by pyridine in the case of some coals[4]. These results suggest that either there exists a set of non-covalent interactions unperturbed by pyridine but disrupted by the mixed solvents or that the mixed solvents are degrading the network and enhancing the extraction yields through some, as yet unknown, chemical reaction.

In the present work we set out to characterize the solution structures of coal extracts to gain insight on the nature of coal-solvent interactions. The characterization of solution structures of dilute mixtures of macromolecules in various solvents is readily attainable using small angle neutron scattering[5-17]. The theory of small angle scattering is well established and the method has been used by many researchers for the purpose of elucidating the configurational state of polymers in solution[6], the structure of asphaltenes in apolar solvents[7-12], the study of proteins[13], as well as dilute coal extract "solutions"[5,14,15]

Neutron scattering is particularly useful in revealing the spatial characteristics of structures composed of low atomic number (Z) elements. This is due to the fact that neutrons, uncharged and with spin (I) = 1/2, interact with a given element through their respective angular momenta. The magnitude of this interaction has no correlation with Z. X-rays, on the other hand, interact with the electronic shell surrounding the nuclei and the magnitude of the coherent scattering amplitude varies as a strong function of Z. Although lighter elements are nearly "invisible" to X-rays, the unique nature of the interaction of the neutron with spin (I) > 0 nuclei results in the coherent scattering cross-section of low Z elements being similar in magnitude to that of many of the higher Z elements[16]; e.g. deuterons scatter neutrons as efficiently as gold.

In the following the results of small angle neutron scattering (SANS) experiments are described in reference to assessing the solution structure of solvent extract "solutions" from a number of coals. The goal of this study is to identify features or characteristics of the mixtures which may highlight the mechanism behind the exceptional solvating capabilities of the mixed solvents as compared with other polar solvents such as pyridine. For the present study we chose a lignite (APCS No. 8), a sub bituminous C rank coal (APCS No. 2), a High volatile bituminous coal (APCS No. 3), and a medium volatile bituminous coal (APCS No. 1) (see Table I).

In addition to characterizing the solution structure of the neat extracts, O-methylated extracts were also studied. The purpose of O-methylation was to neutralize the predominant interaction between coal and pyridine. The medium volatile coal was not O-methylated.

Experimental Section

Solvent Extraction: In the case of pyridine extraction, approximately 5 grams of 100 mesh coal was extracted with pyridine in a Soxhlet extraction apparatus for periods exceeding 24 hours. The extract was separated from the solvent using roto-evaporation. The extractability of the Upper Freeport (UF) coal in the mixed solvent (NMP/CS_2) is over twice that in pyridine as is presented in Table I. Extraction of the Upper Freeport coal (APCS No. 1) with NMP/CS_2 follows the procedure of Iino et al.[4] with minor

modifications. Approximately 5 grams of 100 mesh APCS No. 1. was stirred in 150 ml of a 1:1 mixture (by volume) of n-methyl-2-pyrrolidinone (NMP) and carbon disulfide (CS_2) (mixed solvent, MS) for approximately 6 hours. The solvent extract was decanted and then centrifuged up to 14 K rpm to sediment out any entrained solids.

Throughout the paper below, the various soluble fractions from different coals are designated as presented in Table II.

Small Angle Neutron Scattering: Solutions of the extracts (5 wt.%) were prepared by mixing dry extract with either of the per-deuterated solvents. This concentration was selected to yield sufficient scattering intensity without introducing scattering intensity due to interparticle interactions. Previous work on the SANS behavior of coal extract solutions in pyridine exhibited no dependence on scattering behavior with solvent concentration (at 1, 5, and 10 wt. %) other than a linear increase in incoherent and coherent scattering intensity with increasing wt. % of extract[5].

Solutions were contained in Suprasil cylindrical cells with a 2 mm path length (volume = 0.7 ml) for the SANS analysis. SANS data were measured at the Intense Pulsed Neutron Source of Argonne National Laboratory, using the Small Angle Diffractometer (SAD). This instrument uses pulsed neutrons derived from spallation with wavelengths in the range of 1-14 Å and a fixed sample-to-detector distance of 1.54 meters. The scattered neutrons are measured using a 64 x 64 array of position sensitive, gas filled, 20 x 20 cm^2, proportional counters with the wavelengths measured by time-of-flight by binning the pulse to 67 constant $\Delta t/t = 0.05$ time channels. The size range in a SANS experiment is constrained by both the geometry of the instrument and the wavelength of the neutrons which determine the working range of momentum transfer Q,

$$Q = 4\pi\lambda^{-1} \sin\theta \qquad (1)$$

where θ is half the Bragg scattering angle and λ is the wavelength of the neutrons. Given the characteristics of the SAD[17] at the Intense Pulsed Neutron Source (IPNS), useful SANS data in the Q range of 0.006-0.25 $Å^{-1}$ can be obtained in a single measurement. The reduced data for each sample is corrected for the backgrounds from the instrument, the Suprasil cell, and the solvent as well as for detector nonlinearity. Data are presented on an absolute scale by using the known scattering cross-section of a silica gel sample. The absolute cross-section for this sample has been measured at the SANS instrument at ORNL. Standard Guinier analysis in the region of $QR_g < 1.0$ can be used to extract the radius of gyration, R_g and I(0) values by using the equation below.

$$I(Q) = I(0)\exp(-Q^2 R_g^2/3) \qquad (2)$$

R_g is the root-mean-squared distance of all of the atoms from the centroid of neutron scattering length density of the particle and I(0) is the absolute scattering cross-section at Q=0 which is defined as follows.

$$I(0) = N_p(\rho - \rho_s)^2 V^2 \qquad (3)$$

Here N_p corresponds to the number density of particles, V is the volume of the particle, and ρ and ρ_s are the scattering length densities of the particle and the solvent, respectively. The absolute scattering data of the silica gel standard give $R_g = 44.7 \pm 0.2$ Å and I(0) = 70 cm^{-1}. The magnitudes of R_g and I(0) for this sample are routinely measured in the same Q region and are used to determine scale factors to place the scattering data on an absolute scale in units of cm^{-1}.

RESULTS

SANS of Soluble Fractions in Organic Solvents:

The SANS data, on an absolute scale, for each coal extract in pyridine-d5 is presented in Figures 1-4, where the intensity of the scattered neutrons I(Q) is plotted against the magnitude of the momentum transfer (Q); note that all of the plots are log-log. The SANS data for UF-PyS/dPy, UF-MS/dPy and UF-MS/dM solutions on an absolute scale are presented in figure 5.

The scattering behavior of the lowest rank coal (APCS No. 8) (Figure 1) exhibits power law scattering behavior in the low Q region; the power law exponent is 2.13 for the

untreated extract and 2.29 for the O-methylated. Similar behavior is observed for the sub bituminous extract (APCS No. 2) (Figure 2), with exponents of 1.79 and 2.46, for the untreated and O-methylated extracts, respectively. The high volatile C rank coal exhibits scattering behavior that is "bounded" at low Q for the untreated extract, but exhibits power law scattering at low Q in the O-methylated case (d = 1.7)(figure 3). The medium volatile bituminous coal (APCS No. 1) exhibits scattering behavior that is remarkably similar to that of the (APCS No. 3) (Figure 4). The scattering behavior of the medium volatile coal (APCS No. 1) in the mixed solvent (Figure 5) exhibits only incoherent scattering, i.e. there are no large structures in this particular system.

Discussion

In a number of liquid-phase systems there exist random solution structures that exhibit scattering behavior resulting from self similar or fractal topology. An elegant theory, formulated by Freltoft et al [8], accounts for power law scattering behavior, with $d <$ 3.0, to systems with mass fractal characteristics. Such solution structures are aggregates with structure factors governed by interparticle correlations which decay exponentionally from the center of the aggregate. Thus, changes in *d*, as seen in figures 1-3 reveal changes in the density of the mass fractal aggregates.

In the case of APCS No.s 3 and 1, in pyridine, aggregates also exist, however, they do not exhibit mass fractal characteristics, rather they are readily described using the Guinier approximation. Incidently, The remarkable similarity between the SANS behavior of the two extracts exhibited in Figure 4 strongly suggests that, in both the IL-PyS/dPy and UF-PyS/dPy samples, the molecular aggregates are nearly identical in their chemical composition, size, shape, and number density.

In complete contrast to the aforementioned results, the solution of mixed solvent solubles in NMP/CS_2 (UF-MS/dM) exhibits virtually no coherent scattering intensity across the accessible Q range of the SAD. SANS analysis of the UF-MS/dM solution, therefore, reveals a well dispersed "molecular" solution of small particles. The fact that aggregation does not occur in UF-MS in NMP/CS_2 indicates that the mixed solvent solvates the extractable molecules much more effectively than pyridine, a result which is clearly consistent with the observation of overall enhanced extractability.

The presence of aggregated structures in solutions of coal extracts with pyridine is contradictory to the hypothesis that pyridine is an exceptionally good solvent for coal in a thermodynamic sense. Although, pyridine clearly exhibits a strong interation with acidic functional groups in coal, in the case of coal extracts, pyridine does not appear to have exceptional solvating capabilities. The clustering or aggregation, clearly evident in all of the pyridine solutions suggests that coal-pyridine interactions may not be sufficient to solvate all non-covalently bound material in coal. This implies that the limits in extractability may be the result of limits in pyridines solvating capability, rather than limits dictated by a covalently cross-linked, "infinite", macromolecular network.

Acknowledgments

The neutron scattering experiments were performed at the Intense Pulsed Neutron Source at Argonne National Laboratory. The authors gratefully acknowledge the help of Denis Wozniak of IPNS, Argonne National Laboratory. Insightful discussions related to the mixed solvent/Upper Freeport system with Profs. Masashi Iino and Toshimasa Takanohashi of the Institute of Chemical Reaction Science, Tohoku University, Sendai Japan, are greatly appreciated. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract No. W-31-1090ENG-38. The Intense Pulse Neutron Source is a Department of Energy supported facility.

References

(1) van Krevelan, *Coal*, Third Edition, Elsevier, Amsterdam, 1993, 979.
(2) Larsen, J. W.; Green, T. K.; Kovac, J., *J. Org. Chem.*, 1985, **50**, 4729
(3) Painter, P. C.; Park, Y.; Coleman, M. M., *Energy & Fuels*, 1988, **2**, 693-702
(4) Iino, M.; Takanohashi, T.; Ohsuga, H.;Toda, K., *Fuel*, 1988, **67**, 1639-1647
(5) Cody, G. D.; Thiyagarajan, P.; Botto, R. E.; Hunt, J.E.; Winans, R. E., *Energy & Fuels*, 1994, **8**, 1370-1378
(6) Bates, F. S., *J. Appl. Cryst.*, 1988, **21**, 681.
(7) Herzog, P.; Tchoubar, D.; Espinat, D., *Fuel*, 1988, **67**, 245
(8) Ravey, J. C.; Ducoret, C.; Espinat, D., *Fuel*, 1988, **67**, 1560.
(9) Overfield, R. E., Sheu, E. Y.; Sinha, S. K.; Liang, K. S. *Fuel Sci. Technol. Int*, 1989, **7**, 611.
(10) Senglet, N.;Williams, C.; Faure, D.; Des Courieres, T.; Guilard, R. *Fuel*, 1990, **69**, 72
(11) Storm, D. A.; Sheu, E. Y.; DeTar, M. M. *Fuel*, 1993, **72**, 977.
(12) Thiyagarajan, P. Hunt, J. E., Winans, R. E., Anderson, K. B.; Miller, J. T. *Energy & Fuels*, 1995, **9**, 829.

13) Stuhrmann, H. B.; Miller, A. *J. Appl. Cryst.*, 1978, **11**, 325.
(14) Ho, B.; Briggs, D. E. *Colloids Surf.*, 1982, **4**, 285.
(15) Triolo, R.; Child, H. R. *Fuel*, 1984, **63**, 274.
(16) Bacon, G. E. in *Neutron Diffraction*, Clarendon Press, Oxford, 1975, pp.38-40
(17) Thiyagarajan, P.; Epperson, J. E.; Crawford, R. K.; Carpenter, J. M.; Hjelm, R. P. In *Proceedings of International Seminar on Structural Investigations on Pulsed Neutron Sources*; Dubna, 1993; pp 194.
(18) Freltoft, T.; Kjems, J. K.; Sinha, S. K., *Phys. Rev. B*, 1986, **33**, 269

Table I

Samples and Their Physical Characteristics

Sample	Rank	%C*	%H	%0	%S	%E(NMP/CS_2)**	%E(Pyr)***
APCS No. 8	Lignite	73	4.8	20	0.8	NA	15.0
APCS No. 2	Sub.bit	75	5.4	18	0.6	NA	29.0
APCS No. 3	HvC	78	5.0	14	4.8	NA	29.0
APCS No. 1	mv	86	4.7	8	2.3	56.0	25.5

*Dry ash free basis
**percent extractable (wt.) in NMP/CS_2
***percent extractable (wt.) in pyridine

Table II

Sample Designations

Sample: Solvent	Lignite (Lig)	Sub.bit (Sub)	HvC Bit (HV)	Med. Vol.(MV)
Pyridine	Lig-PyS/dPy*	Sub-Pys/dPY	HV-PyS/dPy	MV-PyS/dPy
NMP/CS2	-	-	-	MV-PyS/dM**

* where PyS - pyridine *solubles*, *dPY-deuteropyridine*
** where dM - perdeutero-n-methyl-pyrrolidinone and carbon disulfide

Figure Captions.

Figure 1: Absolute differential SANS cross-section of APCS No. 8 pyridine extract 5 % (wt.) in pyridine D5, Untreated (filled) and O-methylated (unfilled).

Figure 2: Absolute differential SANS cross-section of APCS No. 2 pyridine extract 5 % (wt.) in pyridine D5, Untreated (filled) and O-methylated (unfilled).

Figure 3: Absolute differential SANS cross-section of APCS No. 3 pyridine extract 5 % (wt.) in pyridine D5, Untreated (filled) and O-methylated (unfilled).

Figure 4: Absolute differential SANS cross-section of APCS No.1 pyridine extract 5 % (wt.) dispersed in pyridine-D5 (filled o) and APCS #.3 pyridine extract 5 % (wt.) dispersed in pyridine-D5 (o).

Figure 5: Absolute differential SANS cross-section of APCS No.1 pyridine extract 5 % (wt.) dispersed in pyridine-D5 (Square), APCS No. 1 pyridine extract 5 % (wt.) in NMP/CS_2 (filled o) APCS No. 1 NMP/CS_2 extract 5 % (wt.) in NMP-D9/CS_2 ((o).

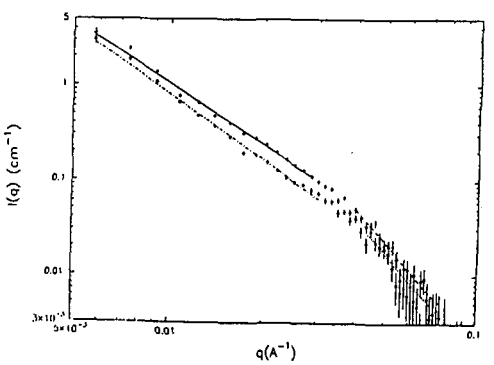


Figure 1

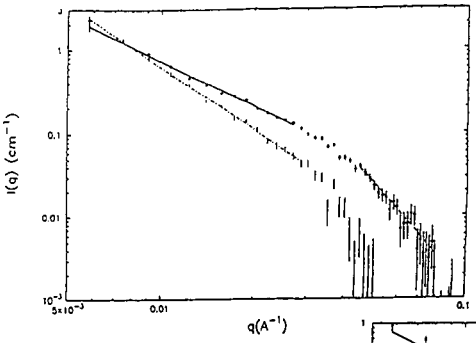
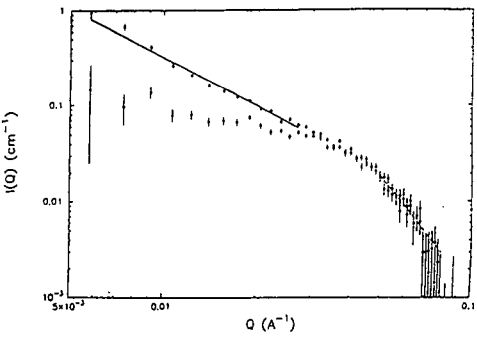


Figure 2

Figure 3



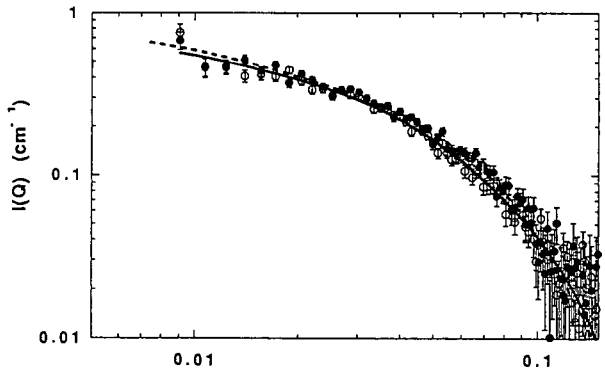


Figure 4

Figure 5